
**Faculty of Resource Science and Technology**

# Synthesis and Characterization of Banana-Shaped Liquid Crystals

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## DECLARATION

I hereby declare that no portion of this dissertation has been submitted in support of an application for another degree of qualification of this or any other university or institution of higher learning.

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**Table of Contents** **Page**

**List of Abbreviations**

| | |
|---|---|
| DCM | dichloromethane |
| FTIR | Fourier Transform Infrared (spectroscopy) |
| HCl | hydrochloric acid |
| IR | infrared (spectroscopy) |
| $K_2CO_3$ | potassium carbonate |
| KOH | potassium hydroxide |
| MEK | methyl ethyl ketone or butanone |
| NaH | sodium hydride |
| NMR | nuclear magnetic resonance (spectroscopy) |
| TBAI | tetrabutylammonium iodide |
| THF | tetrahydrofuran |
| TLC | Thin layer chromatography |
| UV | ultraviolet |

**List of Tables** **Page**

**List of Figures** **Page**

**List of Schemes** **Page**

# Synthesis and Characterization of Banana-Shaped Liquid Crystals

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## ABSTRACT

This study is mainly to synthesize liquid crystals potential compounds derived from chalcone derivatives *via* esterification. New homologues series of banana-shaped liquid crystals (**6a-6c**) have been successfully synthesized *via* esterification based on modifications that have been made on model study (**31**). Initial steps were involving preparation of 4-alkoxybenzaldehydes (**3a-3c**) through etherification prior to chalcone bearing long alkyl chain ($C_{10}$, $C_{12}$, $C_{14}$) (**4a-4c**) synthesis *via* Claisen-Schmidt reaction. Isophthaloyl dichloride was chosen as a starting material to react with alkylated hydroxyl chalcones (**4a-4c**) to form banana-shaped or bent-core liquid crystals properties. The compounds were characterized by IR, $^{1}$H NMR and $^{13}$C NMR spectroscopy.

**Keywords**: Banana-shaped liquid crystals, 4-alkoxybenzaldehyde, chalcone derivatives, isophthaloyl dichloride

## *ABSTRAK*

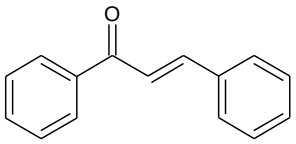
*Kajian ini bertujuan untuk mensintesis kristal cecair berbentuk pisang berdasarkan terbitan kalkon melalui proses pengesteran. Sekumpulan siri homolog baru bagi kristal cecair berbentuk pisang (**6a-6c**) telah disintesis dengan jayanya berdasarkan pengubahan yang telah diaplikasikan pada model yang dikaji (**31**). Pada permulaan, 4-alkoksibenzaldehid (**3a-3c**) telah disintesiskan terlebih dahulu melalui pengeteran untuk penyediaan kalkon yang berantai alkil panjang (**4a-4c**) melalui tindak balas Claisen-Schmidt. Isofataloil klorida dipilih sebagai bahan permula untuk bertindak balas dengan alkylated hidroksil kalkon ($C_{10}$, $C_{12}$, $C_{14}$) (**4a-4c**) dalam penghasilan kristal cecair berbentuk pisang. Pencirian sebatian tersebut telah dilakukan menggunakan spektroskopi IR, $^{1}$H NMR dan $^{13}$C NMR.*

***Kata kunci:*** *Kristal cecair berbentuk pisang, 4-alkoksibenzaldehid, terbitan kalkon, isofataloil klorida*

## 1. Introduction

### 1.1 Chalcone

Chalcone (**1**) is also known as 1,3-diphenyl-2-propene-1-one or benzylideneacetophenone. Chalcone is a type of compound that is presence naturally in most of the plants and it is found to be the intermediate precursor of flavonoids and isoflavonoids (Vincenzo *et al.*, 2000). The structure of chalcone is different from the others members of the flavonoids family as chalcone contains open-chain analogs compared to the other family's members (Echeverriva *et al.*, 2009). The two aromatic rings in chalcones are joined together by a three carbon α,β-unsaturated carbonyl system. Due to the presence of conjugated double bonds in both benzene rings of chalcones, a completely delocalized π-electron system in chalcones is created. As a result, chalcones possess moderately low redox potentials and a higher possibility of undergoing electron transfer reactions (Patil *et al.*, 2009).




**1**

**Figure 1**: General structure of chalcone

Chalcone is very common compound that can be found naturally in plants, starting from ferns to higher plants (Mark *et al.*, 1991). Over the years, chalcones have been extensively studied for their wide range of biological activities, including bacteriostatic, fungistatic, antiparasitic, cardiovascular, antitumor, anticancer, anti-inflammatory, antileishmanial, antitubercular, and antifungi activities and they have been reported to have various biological properties among flavonoids (Ceylan & Findik, 2009; Echeverria *et al.*, 2009). These pharmacological properties of chalcones are mainly caused by the presence of both α,β-unsaturation and an aromatic ring. Chalcone is also very important as a Michael acceptor in organic syntheses (Ceylan & Findik, 2009). The introduction of alkyl chains

onto chalcone derivatives was reported to have antibacterial activities where the inhibition activity was concentration dependant (Ngaini *et al.*, 2009).

Apart from biological properties, others studies on chalcones has been reported for photochemical properties as well as for liquid crystal photoalignment layer (Makita *et al*., 1998). Cho *et al*. (2003) reported that polymerizable liquid crystal molecule which containing two photoreactive chalcone units have the photoimaging ability. Other studies were also proved that chalcone-epoxy polymer system with chalcone group as repeating unit have the capability to retard the decaying behaviour of photochromism most efficiently resulting from the steric hindrance after UV irradiation (Lee *et al*., 2004).

### 1.2 Liquid Crystals

Liquid crystal is an intermediate state of a matter, which is in between the liquid and the crystal. Molecules which possess liquid crystals properties are summarized as they have the anisotropic shape and crystallinity with respect to elongated and flat segments such as benzene rings. It is also has a rigid backbone containing double bonds which defines the long axis of the molecule. The presence of strong dipoles and easily polarized group in the molecules are significant for liquid crystals properties, whereas the groups attached to the extremities of the molecules are less significant in liquid crystals.

### 1.3 Banana-shaped Liquid Crystals / Bent-core Liquid Crystals

There are many types of liquid crystals. Banana-shaped liquid crystal is one of the examples. The first achiral banana-shaped compounds were synthesized in 1993 by Matsunaga *et al*.. However, only mesomorphic properties of the compounds were indicated during that time. Further studies have been done on the ferroelectric and antiferroelectric

properties in the banana-shaped liquid crystals. Banana-shaped liquid crystals have been identified as interesting compounds due to their unexpected electro-optical properties, polarity and chirality (Rouillon *et al.*, 2001). Niori *et al.* (1996) revealed the unusual ferroelectric behaviour of liquid crystals based on achiral banana-shaped molecules and the ability of the banana-shaped molecules to show chirality to the system without having any chiral carbons in the structure (Ros *et al.*, 2005). The chiral nonlinear optic effect shown in achiral bent-core molecules is due to the interaction between polarity and chirality (Takezoe & Takanishi, 2006). The polarity, rigidity and the length as well as the terminal chain of the structures are found to be able to cause certain effects on the bending angle of the liquid crystal structures. The banana-shaped mesophases synthesization is based on the appropriate combination between rigid bent-core units with terminal chains (Ros *et al*., 2005). There is a research found that the homologues series with the same core and increasing number of chain length are responsible in the contribution of the phase sequence B6-B1-B2 (Subala *et al.*, 2011).

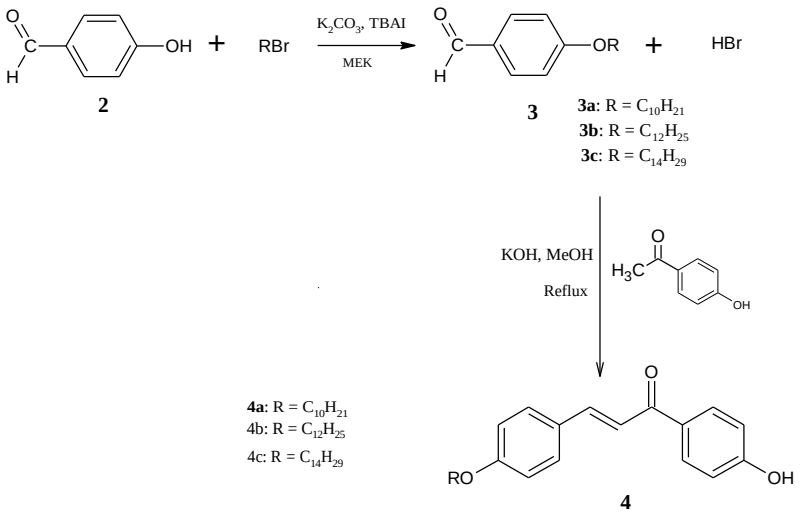
Therefore, in this research we propose to prepare banana-shaped compounds derived from chalcone bearing long alkyl chains to achieve better liquid crystal properties.

### 1.4 Objectives

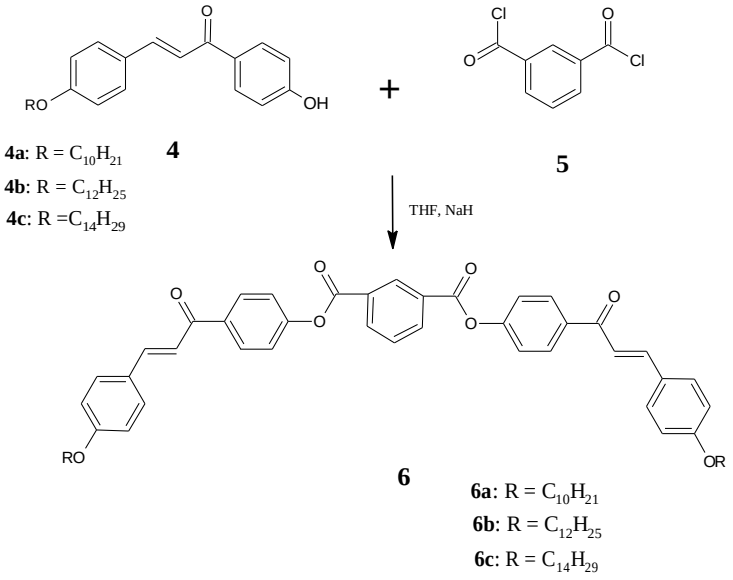
Based on the literature precedents, the objectives of this study are:

1) to synthesize hydroxylated chalcone bearing flexible side chain ($C_{10}$, $C_{12}$, $C_{14}$) (Scheme 1).
2) to synthesize banana-shaped liquid crystal by esterification of chalcone derivatives with isophthaloyl dichloride (Scheme 2).

3) to chacterize the synthesized compounds with $^{1}H$ NMR, $^{13}C$ NMR, and Fourier Transform Infra Red Spectrophotometer (FTIR).




**Scheme 1**: Proposed reaction of chalcone derivatives *via* Claisen-Schmidt condensation process




**Scheme 2**: Proposed reaction of banana-shaped liquid crystal synthesis *via* esterification process

## 2. Literature Review

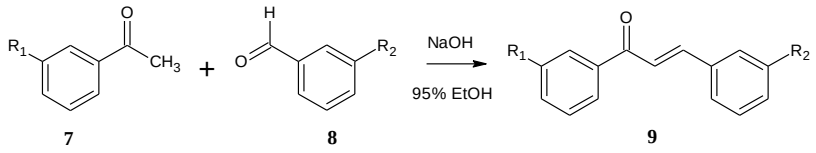
### 2.1 Chalcones

Chalcone is characterized by the yellow colour in appearance and have a boiling point of 345°C (653°F). It has melting point of 54°C (129.2°F) and soluble in cold water.

### 2.2 Synthesis of Chalcones

Chalcone is the main precursors for the synthesis of various flavonoids and can be changed easily to other classes of flavonoids using different reagents and conditions (Jamil, 2006). In the natural formation, chalcone is catalysed by chalcone synthase (Ferrer *et al.*, 1999). There are several methods that can be used to synthesize chalcones in laboratory. These methods include Claisen-Schmidt condensation (Jamil, 2006), direct Friedel-Crafts acylation (Jamil, 2006) and Suzuki reaction (Eddarir *et al*., 2003).

Claisen-Schmidt condensation is the most common and convenient method for chalcones synthesis in laboratory. Claisen-Schmidt condensation is also known as cross aldol condensation which involves the condensation reaction between aldehyde and ketone in the presence of base or acid catalyst. Chalcones are formed by Claisen-Schmidt condensation of appropriate benzaldehyde and acetophenone in the presence of aqueous alkaline bases followed by dehydration (Patil *et al*., 2009). This reaction involves condensation of a C6-C2 unit, substituted acetophenone and a C6-C1 unit, benzaldehyde derivatives to obtain chalcone with bearing A-ring substituents provided by the acetophenone (**7**) and B-ring substituents provided by the benzaldehyde (**8**) to produce (**9**) as shown in Scheme 3 (Jamil, 2006). The reaction is normally conducted at 50°C over a few hours.

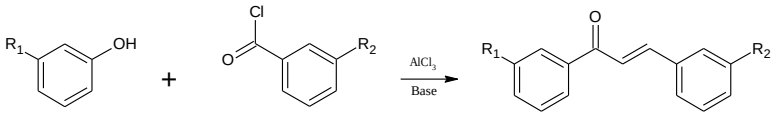



**7** **8** **9**

$R_1$ = alkyl group; $R_2$ = alkyl group

**Scheme 3**: Chalcone synthesis by Claisen-Schmidt condensation

Another method to synthesize chalcones (**12**) is by Friedel-Crafts acylation with the presence of Lewis acid, $AlCl_3$. Phenol (**10**) becomes the A-ring whereas the acylating agent (**11**) provides both the B-ring carbon and the three-carbon bridge to form the C6-C3-C6 unit (Jamil, 2006). The reaction is shown in Scheme 4.

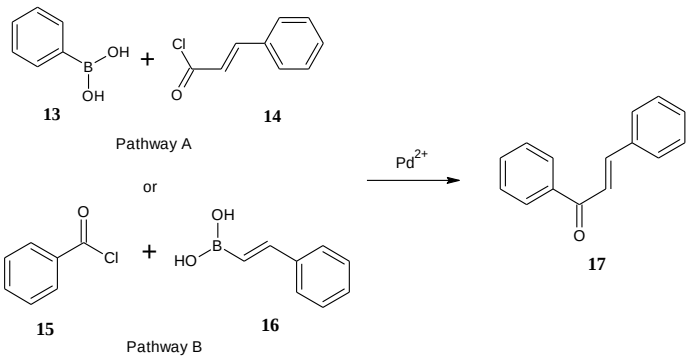



**10** **11** **12**

$R_1$ = alkyl group; $R_2$ = alkyl group

**Scheme 4**: Chalcone synthesis *via* Friedel-Crafts acylation of a phenol

Besides Friedel-Crafts acylation, other method for the synthesis of chalcones is *via* Suzuki reaction either between phenylboronic acids (**13**) and cinnamoyl chlorides (**14**) (Pathway A) or between benzoyl chlorides (**15**) and phenylvinylboronic acids (**16**) (Pathway B) to afford chalcone (**17**) (as shown in Scheme 5) (Eddarir *et al*., 2003). The reactions were performed with the present of palladium catalyst to afford chalcone in good yield.

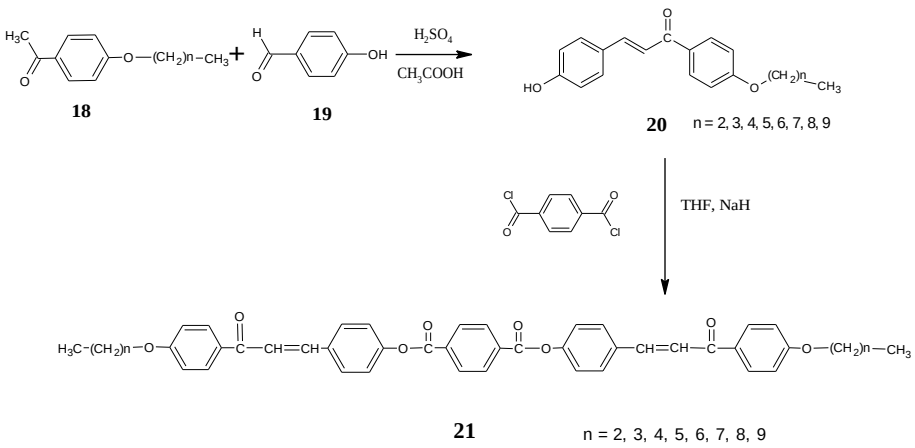



**13** **14** **15** **16** **17**

**Scheme 5**: Synthesis of chalcones by Suzuki reaction

## 2.3 Synthesis of Chalcone Derivatives and Application

In 2007, series of mesogenic compounds based on chalcone units were synthesized for photoreaction studies (Chang *et al.*, 2007). In their work, compounds which contain two chalcone units connected to a benzene ring through ester linkages were synthesized and becoming a part of a rigid rod. The synthesized compounds were differed by their number of alkyloxy tails connected to the two chalcone units through ether linkages. These chalcones were then used to synthesize linear chalcone esters (**21**) by reacting them with benzene-1,4-dicarbonyl dichloride in the presence of sodium hydride (95%) as shown in Scheme 6. Liquid crystal phases were shown by these compounds with two photoreactive chalcone units.

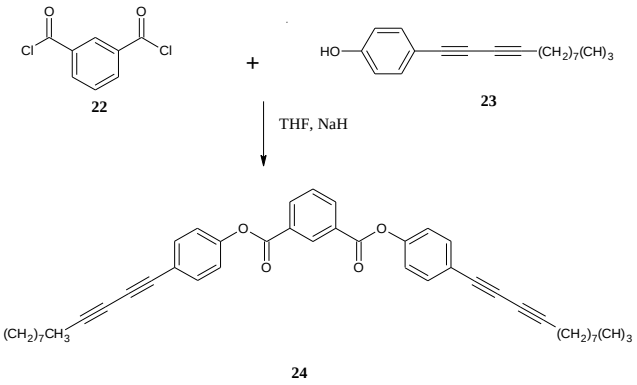



**Scheme 6**: Structure of linear chalcone ester

## 2.4 Esterification *via* Benzene-1,3-dicarbonyl dichloride

Apart from using benzene-1,4-dicarbonyl dichloride in the synthesis of linear chalcone ester through esterification, there was a research done by using benzene-1,3-dicarbonyl dichloride in esterification reaction. In 2003, Cho and coworker have synthesized a bent-shaped mesogenic compound with two diacetylenic groups (**24**) by an esterification reaction of benzene-1,3-dicarbonyl dichloride (**22**) with 1-(4-hydroxyphenyl)-4-

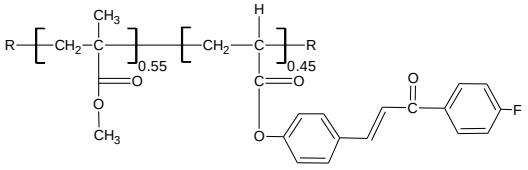
octylbutadiyne (**23**) in THF with the presence of a sodium hydride catalyst. The reaction is shown in Scheme 7. Compound (**24**) was reported for the study of thermal behavior and polymerization (Cho *et al.,* 2003).




**Scheme 7**: Esterification of benzene-1,3- dicarbonyl dichloride

## 2.5 Photochemical Properties of Chalcone

In 2003, Cho *et al.* reported on a photopolymerizable liquid crystal molecule which consists of two photoreactive chalcone units. In their work, photopolymerization by irradiation through a photomask was found to generate an excellent patterned image, which is caused by the [2+2] addition reaction of chalcones in irradiated region. According to Lee *et al.* (2001), the photoreactions of polymers with chalcone groups based on poly[(4-acryloyloxy-4'-fluorochalcone)-co-(methyl methacrylate)] (**25**) (as shown in Figure 2) with exposure to linearly polarized UV light has induced a well-developed homogeneous alignment of nematic liquid crystal perpendicular to the polarization direction of the light.

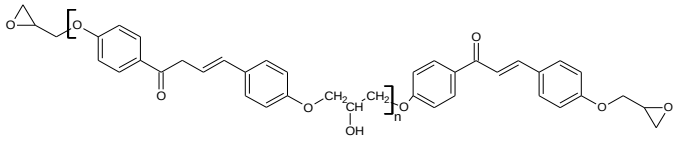



**25**

**Figure 2**: Molecular structure of poly[(4-acryloyloxy-4'-fluorochalcone)-co-(methyl methacrylate)]

The photoinitiated cationic ring-opening polymerization of epoxy compound based on chalcone group has been extensively studied and used in photocrosslinkable polymers as this compound provides high sensitivity to UV radiation (Choi & Cha, 2002).

Most research works were only done on the polymers which contain the chalcone unit in the side chain due to the low solubility of the rigid rod nature of chalcone backbone polymers (Akelah *et al.*, 1992; Akelah *et al.*, 1993; Watanabe *et al.*, 1986). In 2002, Choi and Cha have synthesized a new photoreactive chalcone-epoxy oligomeric (**26**) as shown in Figure 3. The chalcone group was introduced to the main chain unit of the new epoxy compound which possesses high sensitivity towards linearly polarized light (LPL). Photopolymerization and photodimerization properties with photoinitiator were also shown in this compound.



**26**

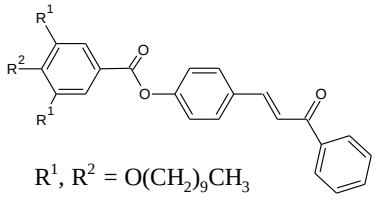
**Figure 3**: Molecular structure of chalcone-epoxy

## 2.6 Liquid crystals

Liquid crystals are intermediate states between crystals and isotropic liquids. Therefore, they possess the intermediate physical properties such as the fluidity of liquids and the anisotropy of crystals (Takezoe & Takanishi, 2006). These unique properties make liquid crystals useful materials for a variety of industrial purposes especially for electronically driven displays. Liquid crystal can exist as both synthetic and natural materials.

Liquid crystals behave distinctly relying on the direction where the electric or magnetic fields are applied with respect to the director. Light is a transverse electromagnetic wave which is made up of mutually perpendicular, fluctuating electric and magnetic fields. Thus, it's properties also depending on the direction of its propagation and polarization regarding the direction in the liquid crystals (Movahed, 2005). Liquid crystals establish birefringence owing to their anisotropic nature in which they having two different indices of refractions. The formation of two different indices of refractions is resulted from which each single index is corresponding to the light polarized parallel to the director and the light polarized perpendicular to the director of liquid crystals respectively.

There are two common techniques that are used for the preparation of liquid crystals monomer. The first technique is done by joining the vinyl groups to both sides of a mesogen *via* flexible spacer; whereas the second technique is through introducing photoreactive groups into mesogens so that parts of rigid rods are formed. These techniques are also applied on chalcone. These parts of rigid rods in liquid crystals molecules are due to the presence of two chalcone units (**27**) or two diacetylene groups (Jang *et al.*, 2007; Lim *et al.*, 2007). Liquid crystals mesophases are categorized into three different types which include chiral calamitic, non-chiral calamitic and discotic mesophases.




**27**

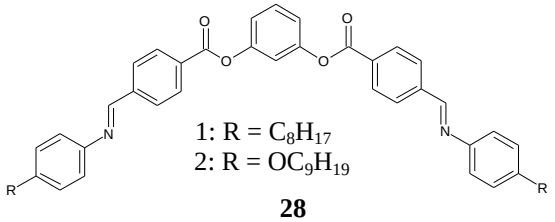
**Figure 4**: Molecular structure of polycatenar compounds comprising a rodlike chalcone unit and a half disklike phenyl group with three long alkoxy chains

## 2.7 Banana-shaped Liquid Crystals / Bent-core Liquid Crystal

Banana-shaped or bent-core liquid crystals have been identified as a very interesting compound from various aspects. The unusual ferroelectric and antiferroelectric properties of liquid crystals based on achiral bent-core molecules is one of the interesting aspects.

Banana-shaped molecule with a bent-core structure in the middle of the mesogenic part was first reported by Niori *et al.* in 1996, with the ability to show ferroelectricity in its smectic phase. The smectic phase formed by banana-shaped liquid crystals is found to be biaxial with the molecules and has a greatest direction of packing into a layer. As a result of this characteristic packing, a spontaneous polarization occurs parallel to the layer and switches on reversal of an applied electric field (Niori *et al.*, 1996). At first, it was recommended that these compounds have a polar smectic A type structure with $C_{2V}$ symmetry in layers. Later, Heppke *et al.* (1997) discovered that the electrically switchable phase showed electro-optic effects and has a tilted smectic C-like structure (Jakli *et al.*, 2001).

Link *et al.* (1997) gave the first evidence for the antiferroelectric properties shown in smectic-C type structure in banana-shaped liquid crystals compounds (**28**). They also pointed out that the ability of the achiral bent molecules to exhibit chirality in smectic phases is owing to the simultaneous director tilt and polar order, in which each smectic layer loses its inversion synmmetry and becomes chiral (Jakli *et al.*, 2001).




**28**

**Figure 5**: Smectic-C type structure of banana-shaped liquid crystals compounds